

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-323552

(43)Date of publication of application : 26.11.1999

(51)Int.Cl.

C23C 14/56
C23C 14/08
G02B 5/30
G09F 9/35
// B32B 9/00
C08J 7/06
C08J 7/06
G02F 1/1335

(21)Application number : 10-339439

(71)Applicant : SUMITOMO CHEM CO LTD

(22)Date of filing : 30.11.1998

(72)Inventor : AZUMA KOJI
SHIMIZU AKIKO
HISHINUMA TAKAHIRO

(30)Priority

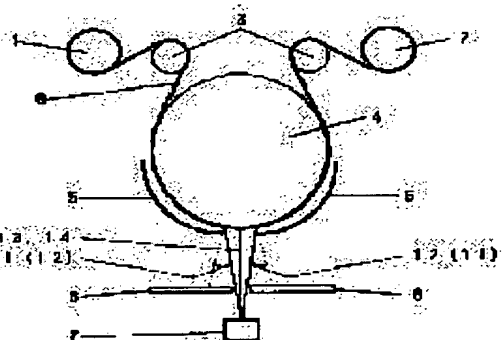
Priority number : 09329016 Priority date : 28.11.1997 Priority country : JP

(54) PRODUCTION OF CONTINUOUS VAPOR-DEPOSITED FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an effective method excellent in mass-productivity, by which a transparent high polymer film is used as a substrate and a continuous vapor-deposited film can be produced in such a manner that the thickness of an inorganic dielectric layer is controlled to a range from several hundreds \AA to several μm , particularly at $>1000 \text{\AA}$; though an optical device using an inorganic dielectric layer obtd. by vapor deposition is very useful.

SOLUTION: At the time of continuously vapor-depositing a vapor-depositing material composed of a nonsublimable inorganic dielectric substance with $\geq 1000^\circ \text{C}$ m.p. on a transparent high-polymer film, on the space between a deposition preventing board 5 prescribing the range of the vapor depositing angle and a vapor depositing source 7 or/and the space between the sticking preventing board 5 and the transparent high polymer film 8, at least one cooling board 6 preventing radiation heat from the vapor depositing source 7 is arranged, and the cooling efficiency is increased to produce the film.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of

rejection]

[Kind of final disposal of application other than the
examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of
rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] A manufacture method of a continuation vacuum evaporatio film of arranging between an adhesion-proof board which specifies a vacuum evaporatio angle range, and sources of vacuum evaporatio or/and an adhesion-proof board, and a cooling plate of at least one sheet that prevents radiant heat from a source of vacuum evaporatio between transparen high polymer films, and gathering and manufacturing cooling effectiveness in case the continuation vacuum evaporatio of the vacuum evaporatio material which consists of an inorganic dielectric whose melting point it is non-sublimability and is 1000 degrees C or more is carried out to up to a transparen high polymer film.

[Claim 2] A manufacture method of a continuation vacuum evaporatio film according to claim 1 that an adhesion-proof board, a cooling plate, and a can roll are cooled with a refrigerant below a room temperature.

[Claim 3] A manufacture method of a continuation vacuum evaporatio film according to claim 1 which an adhesion-proof board and a cooling plate is [a vacuum evaporatio initiation angle] 60 – 85 degrees, and is arranged so that vacuum evaporatio angle width of face may become 10 degrees or more.

[Claim 4] A manufacture method of a continuation vacuum evaporatio film according to claim 1 that a transparen high polymer film is a thermoplastic high polymer film.

[Claim 5] A manufacture method of a continuation vacuum evaporatio film according to claim 4 that a thermoplastic macromolecule is a cellulose system macromolecule, a polycarbonate system macromolecule, a polyarylate system macromolecule, a polyester system macromolecule, an acrylic macromolecule, Pori Sall John, or a polyether ape phone.

[Claim 6] A manufacture method of a continuation vacuum evaporatio film according to claim 1 using a constituent with which a vacuum evaporatio material which consists of an inorganic dielectric contained Ta 2O5 50% of the weight or more, mixture, a constituent which contained TiO2 50% of the weight or more, mixture, a constituent which contained ZrO2 50% of the weight or more, or mixture.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the manufacture method of a continuation vacuum evaporatio film.

[0002]

[Description of the Prior Art] The acid-resisting film which formed the multilayers of an inorganic dielectric thin film on the polyethylene terephthalate film by which biaxial stretching was carried out as a transparen high polymer film in which the vacuum evaporatio layer of the inorganic dielectric used for an optical use was formed, the high polymer film substrate for plastics liquid crystal displays with which orientation formed transparen electric conduction films, such as ITO, on the small high polymer film are known well. These films are manufactured by the sputtering method the thickness per one layer of inorganic dielectrics can raise membranous compactness from a thin thing easily with about hundreds of A.

[0003] Moreover, the Twisted Nematic mold liquid crystal display (it expresses TN-LCD hereafter) in the normally white (it expresses NW hereafter) mode most generally as a liquid crystal display adopted has the serious problem as a display that an angle-of-visibility property is not enough, under the effect of the form birefringence which liquid crystal has. The method using the phase contrast board which it considers as the method of solving this problem greatly, and the optical axis using the method vacuum evaporatio layer of slanting of an inorganic dielectric tended to have inclined from the film normal, and has a positive refractive-index anisotropy is indicated by JP,7-306406,A, WO 96/No. 10773 official report, etc. Moreover, Applied by which the manufacture method of the phase contrast board used for this is quoted by these Optics It is indicated by 28 2466 pages - pages [2482] (1989).

[0004] Since thousands of A - several micrometers and very thick thickness are needed as compared with an antireflection film or a transparen electric conduction film, the phase contrast board of using the sputtering method film production speed is slow single or more figures, as compared with vacuum deposition created with the vacuum deposition used for a liquid crystal display, a quadrant wavelength plate, etc. is not realistic. Moreover, by the creation method by the method vacuum evaporatio layer of slanting of the inorganic dielectric to a glass substrate top which is indicated by these, it is heavy and a chip and mass-production nature are not only missing, but needs heat treatment as the substrate temperature exceeding 200 degrees C, and after treatment for flexibility over long duration.

[0005] Thus, although the optical element using the inorganic dielectric layer obtained by vacuum evaporatio was very useful, it was not known until now about the effective method excellent in the mass-production nature which the thickness of an inorganic dielectric layer can create by the thickness which exceeds especially 1000A from hundreds of A to the thickness of several micrometers, using a transparen high polymer film as a substrate.

[0006] When carrying out the continuation vacuum evaporatio of the vacuum evaporatio material with which this invention persons consist of an inorganic dielectric in view of this condition on a transparen high polymer film, the manufacture method of the continuation vacuum evaporatio film for optical uses of gathering and manufacturing cooling effectiveness can be found out, and it came to complete this invention.

[0007]

[Means for Solving the Problem] That is, in case this invention carries out the continuation vacuum

evaporation of the vacuum evaporation material which consists of an inorganic dielectric whose melting point it is non-sublimability and is 1000 degrees C or more on a transparency high polymer film, it arranges between an adhesion-proof board which specifies a vacuum evaporation angle range, and sources of vacuum evaporation or/and an adhesion-proof board, and a cooling plate of at least one sheet that prevents radiant heat from a source of vacuum evaporation between transparency high polymer films, and relates to a manufacture method of a continuation vacuum-evaporation film of gathering and manufacturing cooling effectiveness.

[0008]

[Embodiment of the Invention] Although it excels in transparency, and it will not be restricted as a transparency high polymer film used for this invention especially if uniform, what consists of a macromolecule thermoplastic at the point of the ease of carrying out of manufacture of a film etc. is used preferably. As a thermoplastic macromolecule, a cellulose system macromolecule, a polycarbonate system macromolecule, a polyarylate system macromolecule, a polyester system macromolecule, an acrylic macromolecule, Pori Sall John, a polyether ape phone, etc. can be illustrated. Although the macromolecule which was excellent in thermal resistance, such as Pori Sall John and a polyether ape phone, especially is advantageous about vacuum evaporation, a cellulose system high polymer film with an available film cheap in cost and uniform and a polycarbonate system high polymer film are also used preferably.

[0009] Moreover, the following formula (1)

$$R_b = (n_{bx} - n_{by}) \times d_b \quad (1)$$

Among [type, in n_{bx} , n_{by} shows the refractive index of the phase leading shaft orientations in the film plane of a transparency high polymer film, and d_b shows the thickness of a transparency high polymer film for the refractive index of the direction of a lagging axis in the film plane of a transparency high polymer film, respectively.] About the use for which it appears and the small thing is [the retardation value in the film plane of the transparency high polymer film shown (R_b)] suitable, a cellulose system high polymer film with a small proper birefringence and an acrylic high polymer film are used especially preferably, and the retardation value (R_b) which is dozens of nm is preferably used for a polycarbonate system high polymer film with a large proper birefringence, a polyester system high polymer film, the poly ape phone film, a polyether ape phone film, etc., when required. When carrying out the method vacuum evaporation of the inorganic dielectric of slanting on a continuation film furthermore, a triacetyl cellulose film with little the heat at the time of vacuum evaporation and deformation of the film by the stress produced for film transport and a polyether ape phone film are used preferably.

[0010] Although the precision extrusion method which can make small residual stress of the solvent cast method or a film can be used as the film production method of a transparency high polymer film, the solvent cast method is preferably used in respect of homogeneity. For producing a film especially with small R_b value, the solvent cast method is desirable.

[0011] Thus, although R_b value of the produced film and the film produced by the solvent cast method especially is small, it comes to have the refractive-index structure where the refractive index (n_{bt}) of the film thickness direction is smaller than the average refractive index (n_{bp}) in a film plane, by the stacking tendency within a field of the macromolecule at the time of film production. For this reason, this transparency high polymer film is the following formula (2) by the form birefringence of the film thickness direction.

$$R'_b = (n_{bp} - n_{bt}) \times d_b \quad (2)$$

(— among a formula, in n_{bt} , n_{bp} shows the average refractive index in a film plane, and d_b shows the thickness of a transparency high polymer film for the refractive index of the thickness direction of a transparency high polymer film, respectively.) — when it comes to have the value whose retardation value (R'_b) of the thickness direction shown is not 0 and has the value whose R'_b is not 0, this transparency high polymer film can also be used as an optical element which has form birefringence by independent [for mere vacuum evaporation / not a base material but independent / its]

[0012] For example, when applying to NW-TN-LCD, it can use as a phase contrast film which has the negative refractive-index anisotropy which has the optical axis used combining the inorganic dielectric

layer which consists of a monolayer toward which it has a positive refractive-index anisotropy, and the optical main shaft inclines from a film normal in the direction of a film normal. At this time, the R'b value of this transparence high polymer film is used in 0nm – about 250nm. Moreover, when the R'b values of a transparence high polymer film run short to a predetermined value, on a transparence high polymer film, the layer containing the inorganic stratified compound indicated by JP,5-196819,A can be formed, and the magnitude of a R'b value can also be adjusted.

[0013] On the other hand, a transparence high polymer film can also be used as a film of the uniaxial orientation nature which has Rb value, and it can obtain by extending the film which produced the film with the solvent cast method or the precision extrusion method in this case using a roll slowing growth method, the tenter extending method, etc. Although Rb value at the time of considering as the film of uniaxial orientation nature is usually set as the range of 100nm or less, it can be adjusted to arbitration if needed. Uniaxial orientation nature contains not only perfect uniaxial orientation but the biaxial orientation nature which has Rb value in a film plane.

[0014] Especially for a limit, although there is nothing, an about 50 micrometers – 500 micrometers thing usually uses, and the thickness of these transparence high polymer films is ****.

[0015] In the case where prepare the method vacuum evaporatio layer of slanting which becomes at least one side of a transparence high polymer film from an inorganic dielectric in this invention, and it considers as a phase contrast film Since it is necessary to make thickness of a vacuum evaporatio layer quite thick so that the retardation value which needs an acid-resisting layer etc. as compared with the case where it forms in the multilayer vacuum evaporatio layer of a dielectric thin film may be discovered, It is desirable to prepare the interlayer who raises adhesion, improves adhesion with a transparence high polymer film, and prevents the crack of a vacuum evaporatio layer. Moreover, this interlayer is effective in improving the thermal resistance of a transparence high polymer film.

[0016] As an interlayer, the poly membrane which consists of acrylic resin, urethane system resin, silicon system resin, cardo resin, or polysilazane is illustrated.

[0017] The method of dissolving in a solvent what was macromolecule-ized as the formation method of these poly membranes, and applying to a transparence high polymer film, the method of macromolecule-izing according to photo-curing or heat curing, after applying the constituent containing a low-molecular monomer or oligomer, and a polymerization initiator to a transparence high polymer film, etc. are used. There is especially no limit in the method of application to a transparence high polymer film, and the well-known methods of application, such as a comma coating method, the die coat method, the direct gravure method, and the bar coat method, can be used.

[0018] The acrylic resin film of an ultraviolet curing mold is preferably used for a cellulose system high polymer film, a polycarbonate system high polymer film, or a polyester system high polymer film, and the polysilazane film of a heat-curing mold can also be used for a high polymer film with high thermal resistance, such as a Pori Sall John and polyether ape phone.

[0019] If the thickness of the poly membrane as an interlayer is thickness by which adhesion amelioration is realized, there will be especially no limit and it will be set as the range of about 0.2 micrometers – 10 micrometers. It is not desirable in order for the adhesion of a transparence high polymer film and an interlayer to fall, if the uniform film by coating will be hard to be obtained if thinner than about 0.2 micrometers, and it becomes thicker than about 10 micrometers.

[0020] Especially if formation of a thin film is possible and it excels in endurance etc. with vacuum deposition as a vacuum evaporatio material which consists of an inorganic dielectric used for this invention, it will not be restricted, but it is desirable in order that the melting point may tend to produce the film which the inorganic dielectric of non-sublimability has precise membraneous quality, and defects, such as a crack, do not generate above 1000 degrees C. As a vacuum evaporatio material which can create the phase contrast film which discovers a positive refractive-index anisotropy by the method vacuum evaporatio of slanting, and discovers especially the optical property toward which the optical main shaft inclined 20 degrees to 70 degrees from the film normal, Ta 2O5 [tantalum pentoxide], The inorganic dielectric which consists of a metallic oxide which uses TiO2 [titanium oxide (IV)] or ZrO2 [zirconium oxide

(IV)] as a principal component tends to discover form birefringence, and is preferably used in respect of excelling in transparency or endurance etc. When forming the vacuum evaporatio layer of the inorganic dielectric which consists of a metallic oxide which uses Ta 2O₅ as a principal component, the metallic oxide which contains Ta 2O₅ 50% of the weight or more, and its mixture can be used. When forming the vacuum evaporatio layer of the inorganic dielectric which consists of a metallic oxide which uses TiO₂ as a principal component, the metallic oxide which contains TiO₂ 50% of the weight or more, and its mixture can be used. When forming the vacuum evaporatio layer of the inorganic dielectric which consists of a metallic oxide which uses ZrO₂ as a principal component, the metallic oxide which contains ZrO₂ 50% of the weight or more, and its mixture can be used. By using these vacuum evaporatio materials, Ta 2O₅ and the vacuum evaporatio layer which uses TiO₂ or ZrO₂ as a principal component are obtained. Although you may use it independently as a vacuum evaporatio material when using Ta 2O₅, the mixture of Ta₂O₅ and Ta (metal) is more desirable from the problem of the ease of vacuum evaporatio, a vacuum evaporatio rate, and radiant heat. Ta₂ — as the mixing ratio of O₅ and Ta (metal) — usually — about 1:0 — it is used in .05–1:1.

[0021] The inorganic dielectric which comes flying at an unnecessary vacuum evaporatio angle can be cut into vacuum evaporatio of a up to [a continuation film] using the vacuum evaporatio equipment which can be vapor-deposited succeeding the film which ** to drawing 1 , and the method of making the film on a can roll (4) vapor-depositing alternatively only the inorganic dielectric which comes flying at a predetermined vacuum evaporatio angle can be used for it. In order to cut the inorganic dielectric which comes flying at an unnecessary vacuum evaporatio angle, an adhesion-proof board (5) and a slit are prepared between the source of vacuum evaporatio (7), and a film (8), and a vacuum evaporatio initiation angle (11) and a vacuum evaporatio termination angle (12) are set up. the vacuum evaporatio which the perpendicular (14) drawn from the source of vacuum evaporatio makes on an intersection with a film plane at this time so that an inorganic dielectric may be efficiently vapor-deposited on a film — a central angle — whenever — (— the source of vacuum evaporatio, an adhesion-proof board, and a film are arranged so that 13) may become between a vacuum evaporatio initiation angle and vacuum evaporatio termination angles. In addition, an angle points out the direction of a film plane normal, and the angle to make.

[0022] When vapor-depositing the inorganic dielectric whose melting point it is non-sublimability with such continuation vacuum evaporatio equipment, and is 1000 degrees C or more, as compared with the case where the melting point vapor-deposits a less than 1000-degree C inorganic dielectric, radiation of the radiant heat from the source of vacuum evaporatio becomes large. Although supply of the radiant heat from the source of vacuum evaporatio in a vacuum evaporatio angle range and the heat by deposition of a up to [the film of vacuum evaporatio material] is unavoidable, it has the influence of the radiant heat from the adhesion-proof board heated by coincidence with the heat from the source of vacuum evaporatio, or a vacuum chamber, and the temperature of a high polymer film rises in the case of the vacuum evaporatio for these heat, and there is risk of the fault of inducing deformation on a film occurring. In order to avoid this, it is desirable to form the cooling plate (6) of at least one sheet between an adhesion-proof board (5) and the source of vacuum evaporatio (7) and/or between an adhesion-proof board (5) and a high polymer film (8) so that not only cooling of the can roll usually adopted but excessive radiant heat may not be added.

[0023] A cooling plate may be installed in parallel with an adhesion-proof board or a can roll side, and a plane thing may be installed so that the effect may become the same. Moreover, it is also effective to install between the locations and high polymer films which are heated with the radiant heat from the source of vacuum evaporatio besides the above-mentioned location etc. Thus, by fully cooling a transparence high polymer film, since a vacuum evaporatio material with the high melting point can also be vapor-deposited with high energy, also when a thick vacuum evaporatio layer is formed, the vacuum evaporatio film excellent in adhesion or endurance can be obtained.

[0024] For example, when manufacturing the method vacuum evaporatio film of continuation slanting for considering as a phase contrast film, method vacuum evaporatio equipment of continuation slanting

which is illustrated to drawing 2 is used. With this equipment, in order to produce an anisotropy in growth of vacuum evaporated material and to make it discover form birefringence efficiently, a vacuum evaporation termination angle is set up so that 60 – 85 degrees and vacuum evaporation angle width of face may be [a vacuum evaporation initiation angle (11)] 10 degrees or more and a vacuum evaporation termination angle (12) may turn into a small angle from a vacuum evaporation initiation angle in an adhesion-proof board (5). the vacuum evaporation which the perpendicular (14) drawn from the source of vacuum evaporation makes on an intersection with a film plane at this time so that an inorganic dielectric may be efficiently vapor-deposited on a film -- a central angle -- whenever -- (as it is in the range of 50 – 80 degrees preferably, the source of vacuum evaporation, an adhesion-proof board, and a film are arranged so that 13) may become between a vacuum evaporation initiation angle and vacuum evaporation termination angles. In the method vacuum evaporation of slanting which used such equipment, since it is necessary to make the bearing rate of a film late since film production effectiveness becomes quite late as compared with the vacuum evaporation from the usual perpendicular direction and the exposure of the radiant heat to a film increases, installation of a cooling plate is more needed.

[0025] The thickness of the inorganic dielectric layer by which the method vacuum evaporation of slanting was carried out when using as a phase contrast film is the following formula (3), although it will not be restricted especially if it is more than the thickness that produces an anisotropy in growth of vacuum evaporated material, and shows form birefringence.

$$R_a = (n_{ax} - n_{ay}) \times d_a \quad (3)$$

Among [type, in n_{ax} , n_{ay} shows the refractive index of the phase leading shaft orientations in the film plane of the method vacuum evaporation layer of slanting, and d_a shows the thickness of the method vacuum evaporation layer of slanting for the refractive index of the direction of a lagging axis in the film plane of the method vacuum evaporation layer of slanting, respectively.] It considers as the thickness from which the predetermined retardation value which comes out and is in the range whose retardation value in the film plane of the method vacuum evaporation layer of slanting of the inorganic dielectric shown (R_a) is about 10nm – 200nm is acquired. Although this thickness changes with whenever [from / of an optical main shaft / a film normal / rate / of the material (inorganic dielectric) to be used / of birefringence, and tilt-angle], the range of it is about 0.2 micrometers – 5 micrometers, and it is usually preferably set up in about 0.4 micrometers – 1 micrometer. The magnitude of whenever [to the film normal of the optical main shaft of an inorganic dielectric layer / tilt-angle], or R_a value, R_b value of a transparency high polymer film, etc. are suitably changed by the use which applies a phase contrast film, and are set up.

[0026] How to repeat vacuum evaporation many times and make it multilayers as a method of obtaining such thickness in the method vacuum evaporation of slanting, is also considered. However, since the interface turns into surface of discontinuity so that it may illustrate to drawing 6 when it grows up as a curved columnar structure which vacuum evaporated material illustrates to drawing 5 by the usual vacuum evaporation from perpendicularly it illustrates to drawing 4 unlike ****, such as an amorphous substance, being formed when the method vacuum evaporation film of slanting is continuously created with such equipment and considers as multilayers, the unnecessary interference color may occur or an optical property may fall greatly in a durability test. For this reason, when forming the method vacuum evaporation layer of slanting succeeding a film top, it is desirable to form the method vacuum evaporation layer of slanting as a monolayer by one vacuum evaporation. In this case, since it is necessary to make the bearing rate of a film still later, a cooling plate is indispensable and it is more desirable to arrange the cooling plate of two or more sheets.

[0027] Since the optical property of a phase contrast film here usually carries out the laminating of the phase contrast film to a polarization film and is used, it means Y value computed by the spectral transmittance under the crossing Nicol's prism measured by the optical system shown in drawing 7 at the time of pasting the lagging axis in the film plane of a phase contrast film together so that it may become 45 degrees to the absorption shaft of a polarization film based on JIS-Z8722. This optical property is decided by R_a value resulting from the refractive-index anisotropy discovered when the optical main shaft inclines 20 degrees to 70 degrees from a film normal, and represents change of a refractive-index anisotropy by

this value change in a durability test. It is desirable that the survival rate of the optical property after leaving it under the high-humidity/temperature of 60-degree-C/90%RH for 96 hours is 70% or more as endurance of a phase contrast film, it is more desirable that it is 80% of survival rates, and it is still more desirable that it is 90% or more of survival rates.

[0028] As the vacuum evaporation method used by this invention, well-known methods, such as electron beam vacuum deposition and the ion plating method, can be used. From the point of productivity and endurance, electron beam vacuum deposition is used preferably.

[0029] Moreover, although it is desirable that it is under the glass transition temperature of a macromolecule, and is under heat deflection temperature preferably as for cooling temperature, such as a cooling plate, an adhesion-proof board, and a can roll, it is more desirable to cool using the refrigerant below a room temperature, for example, 25 degrees C, and it is still more desirable to cool using a refrigerant 0 degree C or less.

[0030] When using the material which the presentation ratio of a tantalum and oxygen may collapse in the case of vacuum evaporation, may serve as hypoxia like Ta₂O₅, and may cause coloring, the technique of introducing oxygen gas into the vacuum evaporation inside of a plane if needed, adjusting the presentation ratio of the oxygen in a vacuum evaporation layer, and raising transparency may be used.

[0031] Since it changes with capacity, exhaust air capacity, etc. of vacuum evaporation equipment, the amount of installation of oxygen gas is chosen suitably. If there are too few amounts of installation, the effect of oxygen installation is not enough, and since an atmospheric pressure may rise and an evaporation rate may fall when reverse has too many amounts of installation, cautions are required. The amount of installation is adjusted so that the atmospheric pressure in equipment generally may not become larger than 10-3 Torr.

[0032] In this invention, since adhesion with the transparency high polymer film which prepared the transparency high polymer film or interlayer of the method vacuum evaporation layer of slanting of an inorganic dielectric and a base material is raised in case the method vacuum evaporation layer of slanting of an inorganic dielectric is prepared on a transparency high polymer film, it is also possible to vapor-deposit, after performing a certain surface treatment to the surface of the side which a transparency high polymer film and an interlayer vapor-deposit. Although not limited especially about the surface treatment method, as what is generally used, heat-treatment in a vacuum, corona treatment, ion bombardment processing, plasma treatment, UV irradiation, an acid, alkali treatment, etc. can be mentioned. The surface treatment method and the degree of processing are suitably chosen by a mechanical strength required for the transparency high polymer film to be used, an interlayer, a vacuum evaporation material, and the phase contrast film finally obtained, endurance, and the optical property.

[0033]

[Effect of the Invention] By this invention, by non-sublimability, and when carrying out the continuation vacuum evaporation of the vacuum evaporation material with which the melting point consists of an inorganic dielectric which is 1000 degrees C or more to up to a transparency high polymer film, When the vacuum evaporation bed depth used especially as a phase contrast film manufactures a thick vacuum evaporation film, in the case The vacuum evaporation film excellent in the adhesion and endurance of a vacuum evaporation layer and a transparency high polymer film of an inorganic dielectric can be manufactured continuously, without the fault of the temperature of a high polymer film rising and a film deforming for the heat at the time of vacuum evaporation, occurring.

[0034]

[Example] Hereafter, although an example explains this invention to details, this invention is not limited to this. In addition, measurement of Ra value in an example and Rb value was performed with the conventional method by the homogeneous light with a wavelength of 546nm using the polarization microscope. Moreover, it asked for whenever [from / of an optical main shaft / a film normal / tilt-angle] with this contractor's conventional method from the tilt-angle dependency of the retardation value (value which deducted the retardation value of a transparency high polymer film when a transparency high polymer film had form birefringence) when making the phase leading shaft in a film plane into an axis of tilt, having assumed that

refractive-index structure was optically uniaxial.

[0035] the lagging axis in the film plane of the phase contrast film by this invention becomes 45 degrees at a durability test to the absorption shaft of a polarization film (SQ-1852AP7, Sumitomo Chemical Co., Ltd. make) -- as -- the transparence high polymer film side of a phase contrast film -- a polarization film -- pasting together -- the method vacuum evaporatio layer side of slanting -- optical -- etc. -- the sample whose magnitude which pasted the glass plate with a thickness of 1.1mm together through the **** acrylic binder is 30mmx30mm was used.

[0036] The spectral transmittance for asking for an optical property measured the absorption shaft of the polarizing prism by the side of incident light, and the polarization film of a sample as parallel in the optical system shown in drawing 6 using the spectroscope (MCPD-2000, Otsuka electronic incorporated company make), and computed Y value based on JIS-Z8722. The rate of Y value after 96-hour neglect was made into the survival rate of an optical property under 60-degree-C90%RH to the initial value of Y value. In addition, the reference of spectral transmittance measured the absorption shaft of a polarizing prism as parallel, made the absorption shaft of a polarizing prism cross at right angles after reference measurement, and measured the sample.

[0037] On the example 1 triacetyl-cellulose film (trade name FUJI TAC SH-80 Fuji Photo Film make and Rb are about 11nm), the acrylic resin of an ultraviolet curing mold was stiffened behind the coat by the comma coating machine, was stiffened by UV irradiation, and the transparence high polymer film which formed the acrylic resin film with a thickness of about 5 micrometers as an interlayer was obtained. The continuation film which carried out the slit of this film to 130mm width of face was obtained. This transparence high polymer film is set to the continuation vacuum deposition inside of a plane of drawing 5 , and it exhausts to atmospheric-pressure 1×10^{-4} Torr. With electron beam vacuum deposition 80 vacuum evaporatio initiation angles, 45 vacuum evaporatio termination angles, and vacuum evaporatio -- a central angle -- whenever -- 60 degrees and a film -- the distance of about 350mm between a vacuum evaporatio center and a substrate Arrange a shield so that it may become, and the adhesion-proof board and the cooling plate of one sheet which prevents the radiant heat from the source of vacuum evaporatio between the sources of vacuum evaporatio are installed. The cooling temperature of 0 degree C of a part for EB gun output [of 6kW], and 0.2m/ of bearer rates, and a can roll, The method vacuum evaporatio layer of slanting which consists of a monolayer with a thickness of 4700A was continuously formed using mixture (the Optron, Inc. make, trade name:OA-100) with Ta (metal) which used Ta 2O5 as the principal component as a vacuum evaporatio material, and the phase contrast film was obtained.

[0038] When viewing estimated the appearance of this phase contrast film, there is also no deformation of the base material by the radiant heat at the time of vacuum evaporatio, and exfoliation of vacuum evaporatio layers, such as a crack, was not accepted, either. Although the retardation value in a film plane of this phase contrast film is 29nm and the optical main shaft was changing succeeding the film thickness direction corresponding to change of the vacuum evaporatio angle at the time of continuation vacuum evaporatio, the value calculated having assumed to be what currently is not changing inclined about 33 degrees from the film normal. When this phase contrast film was covered over the durability test, the survival rate of an optical property was 95%.

[0039] The interlayer who got like example of comparison 1 example 1 is formed, a transparence high polymer film is set to the continuation vacuum deposition inside of a plane of drawing 5 , and surface treatment is exhausted to atmospheric-pressure 1×10^{-4} Torr. With electron beam vacuum deposition 80 vacuum evaporatio initiation angles, 45 vacuum evaporatio termination angles, and vacuum evaporatio -- a central angle -- whenever -- 0 times and a film -- the distance of about 325mm between a vacuum evaporatio center and a substrate A shield is arranged so that it may become. At a part for EB gun output [of 6kW], and 0.2m/ of bearer rates, and the cooling temperature of 0 degree C of a can roll The method vacuum evaporatio layer of slanting which consists of a monolayer with a thickness of 3500A was continuously formed using mixture (the Optron, Inc. make, trade name:OA-100) with Ta (metal) which used Ta 2O5 as the principal component as a vacuum evaporatio material, and the

phase contrast film was obtained.

[0040] When viewing estimated the appearance of this phase contrast film, the base material deformed with the radiant heat at the time of vacuum evaporation, and foaming was also accepted in the TAC side.

Although the retardation value in a film plane of this phase contrast film is 16nm and the optical main shaft was changing succeeding the film thickness direction corresponding to change of the vacuum evaporation angle at the time of continuation vacuum evaporation, the value calculated having assumed to be what currently is not changing inclined about 27 degrees from the film normal. Moreover, when this phase contrast film was covered over the durability test, the survival rate of an optical property was what is inferior as compared with what installed and produced 36% and a cooling plate.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The schematic diagram of the 1st example of equipment for manufacturing the continuation vacuum evaporatio film by this invention.

[Drawing 2] The schematic diagram of the 2nd example of equipment for manufacturing the continuation vacuum evaporatio film by this invention.

[Drawing 3] The schematic diagram of the 3rd example of equipment for manufacturing the continuation vacuum evaporatio film by this invention.

[Drawing 4] The mimetic diagram of the cross section of the film with which the method vacuum evaporatio layer of slanting which consists of a monolayer was formed on the transparence high polymer film which continued using the continuation vacuum evaporation system vapor-deposited from perpendicularly it illustrated to drawing 1.

[Drawing 5] The mimetic diagram of the cross section of the phase contrast film with which the method vacuum evaporatio layer of slanting which consists of a monolayer was formed on the transparence high polymer film which continued using the continuation vacuum evaporation system which performs the method vacuum evaporatio of slanting illustrated to drawing 2 or drawing 3.

[Drawing 6] The mimetic diagram of the cross section of the phase contrast film with which the method vacuum evaporatio layer of slanting which consists of a multilayer was formed on the transparence high polymer film which continued using the continuation vacuum evaporation system which performs the method vacuum evaporatio of slanting illustrated to drawing 2 or drawing 3.

[Drawing 7] The schematic diagram of the optical system for measurement of the optical property of a phase contrast film.

[Description of Notations]

- 1 Continuation Film Volume *****
- 2 Continuation Film Dictation Section
- 3 Guide Roll
- 4 Can Roll
- 5 Adhesion-proof Board
- 6 Cooling Plate
- 7 Source of Vacuum Evaporatio
- 8 Transparence Macromolecule Continuation Film
- 11 Vacuum Evaporatio Initiation Angle
- 12 Vacuum Evaporatio Termination Angle
- 13 Vacuum Evaporatio Center Angle
- 14 Perpendicular Drawn from Source of Vacuum Evaporatio
- 15 The Direction of Film Transport
- 21 Method Vacuum Evaporatio Layer of Slanting Depended on Continuation Vacuum Deposition
- 22 Interlayer
- 23 Transparence High Polymer Film
- 51 Incident Light
- 52 Polarizing Prism by the side of Incident Light

- 53 Polarization Film of Sample for Measurement
 - 54 Phase Contrast Film of Sample for Measurement
 - 55 Glass Plate Which Pasted Sample for Measurement Together
 - 56 Polarizing Prism by the side of Outgoing Radiation Light
 - 57 Hikaru Idei
 - 61 Absorption Shaft Orientations of Polarizing Prism by the side of Incidence
 - 62 Absorption Shaft Orientations of Polarization Film of Sample for Measurement
 - 63 The Direction of Lagging Axis in Film Plane of Phase Contrast Film of Sample for Measurement
 - 64 Angle Which Absorption Shaft Orientations of Polarization Film of Sample for Measurement and the Direction of Lagging Axis of Phase Contrast Film Make (45 Degrees)
 - 65 Absorption Shaft Orientations of Polarizing Prism by the side of Outgoing Radiation Light
-

[Translation done.]

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平11-323552

(43)公開日 平成11年(1999)11月26日

(51)Int.Cl.⁶
C 2 3 C 14/56
14/08
G 0 2 B 5/30
G 0 9 F 9/35
// B 3 2 B 9/00

識別記号

3 2 0

F I

C 2 3 C 14/56
14/08

G 0 2 B 5/30

G 0 9 F 9/35

B 3 2 B 9/00

D

K

3 2 0

A

審査請求 未請求 請求項の数6 O L (全 8 頁) 最終頁に続く

(21)出願番号 特願平10-339439

(22)出願日 平成10年(1998)11月30日

(31)優先権主張番号 特願平9-329016

(32)優先日 平9(1997)11月28日

(33)優先権主張国 日本 (J P)

(71)出願人 000002093

住友化学工業株式会社

大阪府大阪市中央区北浜4丁目5番33号

(72)発明者 東 浩二

大阪府高槻市塚原2丁目10番1号 住友化学工業株式会社内

(72)発明者 清水 朗子

大阪府高槻市塚原2丁目10番1号 住友化学工業株式会社内

(72)発明者 菱沼 高広

大阪府高槻市塚原2丁目10番1号 住友化学工業株式会社内

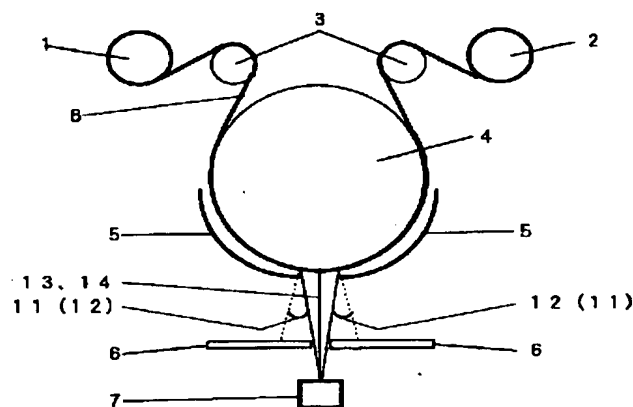
(74)代理人 弁理士 久保山 隆 (外1名)

(54)【発明の名称】 連続蒸着フィルムの製造方法

(57)【要約】 (修正有)

【課題】、蒸着により得られる無機誘電体層を用いた光学素子は非常に有用ではあるが、透明高分子フィルムを基板として用い、かつ無機誘電体層の厚みが数百Åから数μmの厚みまで、特に1000Åを越える厚みで作成できる量産性に優れた有効な方法を提供する。

【解決手段】 非昇華性でかつ融点が1000℃以上である無機誘電体からなる蒸着材料を透明高分子フィルム8上へ連続蒸着する際、蒸着角度範囲を規定する防着板5と蒸着源7の間または／および防着板5と透明高分子フィルム8の間に蒸着源7からの輻射熱を防ぐ少なくとも1枚の冷却板6を配置して冷却効率を上げて製造する連続蒸着フィルムの製造方法。



(2)

1

【特許請求の範囲】

【請求項1】非昇華性でかつ融点が1000℃以上である無機誘電体からなる蒸着材料を透明高分子フィルム上へ連続蒸着する際、蒸着角度範囲を規定する防着板と蒸着源の間または／および防着板と透明高分子フィルムの間に蒸着源からの輻射熱を防ぐ少なくとも1枚の冷却板を配置して冷却効率を上げて製造する連続蒸着フィルムの製造方法。

【請求項2】防着板および冷却板およびキャンロールが室温以下の冷媒により冷却されている請求項1に記載の連続蒸着フィルムの製造方法。

【請求項3】防着板および冷却板が、蒸着開始角度が60度～85度でかつ蒸着角度幅が10度以上となるように配置されている請求項1に記載の連続蒸着フィルムの製造方法。

【請求項4】透明高分子フィルムが、熱可塑性高分子フィルムである請求項1に記載の連続蒸着フィルムの製造方法。

【請求項5】熱可塑性高分子が、セルロース系高分子、ポリカーボネート系高分子、ポリアリレート系高分子、ポリエステル系高分子、アクリル系高分子、ポリサルフォンまたはポリエーテルサルフォンである請求項4に記載の連続蒸着フィルムの製造方法。

【請求項6】無機誘電体からなる蒸着材料が、 Ta_2O_5 を50重量%以上含有した組成物もしくは混合物、または TiO_2 を50重量%以上含有した組成物もしくは混合物、または ZrO_2 を50重量%以上含有した組成物もしくは混合物を用いたものである請求項1に記載の連続蒸着フィルムの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は連続蒸着フィルムの製造方法に関する。

【0002】

【従来の技術および発明が解決しようとする課題】光学用途に用いられる無機誘電体の蒸着層を形成した透明高分子フィルムとしては、二軸延伸されたポリエチレンテレフタレートフィルム上に無機誘電体薄膜の多層膜を形成した反射防止フィルムや、配向が小さい高分子フィルム上にITOなどの透明導電膜を形成したプラスチック液晶表示装置用の高分子フィルム基板などが良く知られている。これらのフィルムは無機誘電体1層当たりの厚みが数百Å程度と薄いことから、容易に膜の緻密性を上げることができるスパッタリング法により製造されている。

【0003】また、液晶表示装置として最も一般的に採用されているノーマリホワイト（以下、NWと表わす）モードのツイステッドネマチック型液晶表示装置（以下、TN-LCDと表わす）は、液晶が有する複屈折性の影響により視野角特性が十分でないという表示装置と

2

して重大な問題を有している。この問題を大きく改善する方法として無機誘電体の斜方蒸着層を用いた光学軸がフィルム法線方向から傾斜した方向にありかつ正の屈折率異方性を有する位相差板を用いる方法が、特開平7-306406号公報およびWO96/10773号公報などに記載されている。また、これに用いる位相差板の製造方法が、これらに引用されているApplied Optics 28巻（1989年）2466頁～2482頁に記載されている。

【0004】液晶表示装置や4分の1波長板などに利用される蒸着法で作成される位相差板は、反射防止膜や透明導電膜と比較して数千Å～数μmと非常に厚い膜厚が必要となるため、蒸着法と比較して製膜速度が1桁以上遅いスパッタリング法を用いることは現実的でない。また、これらに記載されているようなガラス基板上への無機誘電体の斜方蒸着層による作成方法では、重く、柔軟性に欠け、量産性に欠けるだけでなく、200℃を越える基板温度と後処理としての熱処理を長時間にわたって必要としている。

【0005】このように、蒸着により得られる無機誘電体層を用いた光学素子は非常に有用ではあるが、透明高分子フィルムを基板として用い、かつ無機誘電体層の厚みが数百Åから数μmの厚みまで、特に1000Åを越える厚みで作成できる量産性に優れた有効な方法についてはこれまで知られていなかった。

【0006】かかる状況に鑑み、本発明者らは無機誘電体からなる蒸着材料を透明高分子フィルム上に連続蒸着する際、冷却効率を上げて製造する光学用途向けの連続蒸着フィルムの製造方法を見出すことができ、本発明を完成するに至った。

【0007】

【課題を解決するための手段】すなわち本発明は、非昇華性でかつ融点が1000℃以上である無機誘電体からなる蒸着材料を透明高分子フィルム上に連続蒸着する際、蒸着角度範囲を規定する防着板と蒸着源の間または／および防着板と透明高分子フィルムの間に蒸着源からの輻射熱を防ぐ少なくとも1枚の冷却板を配置して冷却効率を上げて製造する連続蒸着フィルムの製造方法に関する。

【0008】

【発明の実施の形態】本発明に用いる透明高分子フィルムとしては、透明性に優れ、均一なものであれば特に制限されないが、フィルムの製造のしやすさなどの点で熱可塑性の高分子からなるものが好ましく用いられる。熱可塑性高分子としては、セルロース系高分子、ポリカーボネート系高分子、ポリアリレート系高分子、ポリエステル系高分子、アクリル系高分子、ポリサルフォン、ポリエーテルサルフォンなどを例示することができる。中でもポリサルフォン、ポリエーテルサルフォンなど耐熱性に優れた高分子が蒸着については有利であるが、コス

(3)

的に安価で均一なフィルムが入手可能であるセルロース系高分子フィルム、ポリカーボネート系高分子フィルムも好ましく用いられる。

【0009】また、下記計算式(1)

$$Rb = (nbx - nby) \times db \quad (1)$$

〔式中、nbxは透明高分子フィルムのフィルム面内の遅相軸方向の屈折率を、nbyは透明高分子フィルムのフィルム面内の進相軸方向の屈折率を、dbは透明高分子フィルムの厚みをそれぞれ示す。〕で示される透明高分子フィルムのフィルム面内のレターデーション値(Rb)が小さいものが適している用途については、固有複屈折が小さいセルロース系高分子フィルム、アクリル系高分子フィルムが特に好ましく用いられ、数十nmのレターデーション値(Rb)が必要な場合には固有複屈折が大きいポリカーボネート系高分子フィルム、ポリエステル系高分子フィルム、ポリサルフォンフィルム、ポリエーテルサルフォンフィルムなどが好ましく用いられる。さらに連続フィルム上に無機誘電体を斜方蒸着する場合には、蒸着時の熱とフィルム搬送のために生じる応力によるフィルムの変形が少ないトリアセチルセルロースフィルムやポリエーテルサルフォンフィルムが好ましく用いられる。

【0010】透明高分子フィルムの製膜方法としては、溶剤キャスト法やフィルムの残留応力を小さくできる精密押出法などを用いることができるが、均一性の点で溶剤キャスト法が好ましく用いられる。特にRb値が小さいフィルムを作製するには溶剤キャスト法が好ましい。

【0011】このようにして製膜されたフィルム、中でも溶剤キャスト法により製膜されたフィルムはRb値は小さいが、製膜時の高分子の面内配向性によりフィルム厚み方向の屈折率(nbt)がフィルム面内の平均屈折率(nbp)よりも小さいという屈折率構造を持つようになる。このため、この透明高分子フィルムはフィルム厚み方向の複屈折性により、下記計算式(2)

$$R'b = (nbp - nbt) \times db \quad (2)$$

〔式中、nbtは透明高分子フィルムの厚み方向の屈折率を、nbpはフィルム面内の平均屈折率を、dbは透明高分子フィルムの厚みをそれぞれ示す。〕で示される厚み方向のレターデーション値(R'b)が0ではない値を有するようになり、R'bが0ではない値を有する場合には、この透明高分子フィルムは単なる蒸着のための基材ではなく、それ単独で複屈折性を有する光学素子として利用することもできる。

【0012】例えば、NW-TN-LCDに適用する場合、正の屈折率異方性を有しかつ光学主軸がフィルム法線方向から傾斜している単一層からなる無機誘電体層と組み合わせて用いられる光学軸がフィルム法線方向にある負の屈折率異方性を有する位相差フィルムとして利用することができる。この時この透明高分子フィルムのR'b値は0nm～250nm程度の範囲で用いられ

4

る。また、透明高分子フィルムのR'b値が所定の値に対して不足する場合には、透明高分子フィルム上に特開平5-196819号公報に記載されている無機層状化合物を含む層を形成してR'b値の大きさを調整することもできる。

【0013】一方、透明高分子フィルムをRb値を有する一軸配向性のフィルムとして用いることもでき、この場合には溶剤キャスト法や精密押出法により製膜したフィルムをロール間延伸法、テンター延伸法などを用いて延伸することにより得ることができる。一軸配向性のフィルムとした場合のRb値は、通常100nm以下の範囲に設定されるが、必要に応じて任意に調整することができる。一軸配向性とは、完全一軸配向だけでなく、フィルム面内にRb値を有する二軸配向性も含むものである。

【0014】これらの透明高分子フィルムの厚みは、特に制限はないが、通常、約50μm～500μmのものが用いられる。

【0015】本発明において、例えば透明高分子フィルムの少なくとも片面に無機誘電体からなる斜方蒸着層を設けて位相差フィルムとする場合などでは、反射防止層などを誘電体薄膜の多層蒸着層で形成する場合と比較して、必要とするレターデーション値が発現するように蒸着層の厚みをかなり厚くすることが必要となるため、密着性を上げて透明高分子フィルムとの密着性を向上し、蒸着層の割れを防止する中間層を設けることが好ましい。また、この中間層は透明高分子フィルムの耐熱性を向上する効果もある。

【0016】中間層としては、アクリル系樹脂、ウレタン系樹脂、シリコン系樹脂、カルド樹脂またはポリシラザンからなる高分子膜が例示される。

【0017】これら高分子膜の形成方法としては、高分子化されたものを溶剤に溶解して透明高分子フィルムに塗布する方法や、低分子モノマーまたはオリゴマーと重合開始剤を含む組成物を透明高分子フィルムに塗布した後光硬化または熱硬化により高分子化する方法などが用いられる。透明高分子フィルムへの塗布方法には特に制限はなく、コンマコート法、ダイコート法、ダイレクト・グラビア法、バーコート法などの公知の塗布方法を用いることができる。

【0018】セルロース系高分子フィルムやポリカーボネート系高分子フィルムやポリエステル系高分子フィルムには紫外線硬化型のアクリル系樹脂膜が好ましく用いられ、ポリサルフォン、ポリエーテルサルフォンなどの耐熱性が高い高分子フィルムには熱硬化型のポリシラザン膜も用いることができる。

【0019】中間層としての高分子膜の膜厚は密着性改良が実現される厚みであれば特に制限はなく、約0.2μm～10μmの範囲に設定される。約0.2μmより薄いコーティングによる均一な膜が得られにくく、ま

(4)

5

た約10 μ mより厚くなると透明高分子フィルムと中間層の密着性が低下するようになるため好ましくない。

【0020】本発明に用いる無機誘電体からなる蒸着材料としては、真空蒸着により薄膜の形成が可能で、耐久性などで優れるものであれば特に制限されないが、融点が1000℃以上で非昇華性の無機誘電体が、膜質が緻密でクラックなどの欠陥が発生しない膜を製膜しやすいため好ましい。特に、斜方蒸着により正の屈折率異方性を発現し、その光学主軸がフィルム法線方向から20度～70度傾斜した光学特性を発現する位相差フィルムを作成できる蒸着材料としてはTa₂O₅〔酸化タンタル(V)〕、TiO₂〔酸化チタン(IV)〕またはZrO₂〔酸化ジルコニウム(IV)〕を主成分とする金属酸化物からなる無機誘電体が複屈折性を発現しやすく、透明性や耐久性に優れるなどの点で好ましく用いられる。Ta₂O₅を主成分とする金属酸化物からなる無機誘電体の蒸着層を形成する場合には、Ta₂O₅を50重量%以上含有する金属酸化物およびその混合物を用いることができる。TiO₂を主成分とする金属酸化物からなる無機誘電体の蒸着層を形成する場合にはTiO₂を50重量%以上含有する金属酸化物およびその混合物を用いることができる。ZrO₂を主成分とする金属酸化物からなる無機誘電体の蒸着層を形成する場合にはZrO₂を50重量%以上含有する金属酸化物およびその混合物を用いることができる。これらの蒸着材料を用いることにより、Ta₂O₅、TiO₂またはZrO₂を主成分とする蒸着層が得られる。蒸着材料として、Ta₂O₅を使用する場合、単独で使用してもよいが、蒸着の容易性、蒸着レート、放射熱の問題からTa₂O₅とTa(金属)の混合物がより好ましい。Ta₂O₅とTa(金属)の混合比としては、通常、約1:0.05～1:1の範囲で用いられる。

【0021】連続フィルム上への蒸着には、例えば図1に示するフィルムに連続して蒸着できる蒸着装置を用いて、不要な蒸着角度で飛来してくる無機誘電体をカットして、キャンロール(4)上にあるフィルムに所定の蒸着角度で飛来してくる無機誘電体のみを選択的に蒸着させる方法を用いることができる。不要な蒸着角度で飛来してくる無機誘電体をカットするためには蒸着源(7)とフィルム(8)の間に防着板(5)やスリットを設け、蒸着開始角度(11)および蒸着終了角度(12)を設定する。この時、無機誘電体が効率良くフィルム上に蒸着されるように、蒸着源から引いた垂線(14)がフィルム面との交点でなす蒸着中心角度(13)が蒸着開始角度と蒸着終了角度の間となるように蒸着源、防着板およびフィルムを配置する。なお、角度はフィルム面法線方向となす角度を指す。

【0022】このような連続蒸着装置で非昇華性でかつ融点が1000℃以上である無機誘電体を蒸着する場合、融点が1000℃未満の無機誘電体を蒸着する場合

6

と比較して、蒸着源からの放射熱の放射が大きくなる。蒸着角度範囲における蒸着源からの放射熱および蒸着物質のフィルム上への堆積による熱の供給は避けることができないが、同時に蒸着源からの熱で加熱された防着板や真空チャンバーからの放射熱の影響もあり、これらの熱のために蒸着の際に高分子フィルムの温度が上昇し、フィルムに変形を誘発するなどの不具合が発生する危険がある。これを回避するためには、通常採用されるキャンロールの冷却だけではなく、余分な放射熱が加わらないように防着板(5)と蒸着源(7)の間および/または防着板(5)と高分子フィルム(8)の間に少なくとも1枚の冷却板(6)を設けることが好ましい。

【0023】冷却板は防着板やキャンロール面に平行に設置してもよいし、平面状のものをその効果が同様となるように設置してもよい。また、上記の場所以外にも蒸着源からの放射熱で加熱される場所と高分子フィルムとの間などに設置することも有効である。このように透明高分子フィルムを十分に冷却することで、融点が高い蒸着材料でも高エネルギーで蒸着できるため、厚い蒸着層を形成した場合にも、密着性や耐久性に優れた蒸着フィルムを得ることができる。

【0024】例えば、位相差フィルムとするための連続斜方蒸着フィルムを製造する場合は、図2に例示するような連続斜方蒸着装置などを用いる。この装置では、蒸着物質の成長に異方性を生じて複屈折性を効率良く発現させるために、防着板(5)を蒸着開始角度(11)が60度～85度、蒸着角度幅が10度以上でかつ蒸着終了角度(12)が蒸着開始角度よりも小さい角度となるように蒸着終了角度を設定する。この時、無機誘電体が効率良くフィルム上に蒸着されるように、蒸着源から引いた垂線(14)がフィルム面との交点でなす蒸着中心角度(13)が蒸着開始角度と蒸着終了角度の間となるように、好ましくは50度～80度の範囲にあるように、蒸着源、防着板およびフィルムを配置する。このような装置を用いた斜方蒸着では、通常の垂直方向からの蒸着と比較して製膜効率がかかなり遅くなるため、フィルムの搬送速度を遅くすることが必要となり、フィルムへの放射熱の照射が増大するため、冷却板の設置がより必要となる。

【0025】位相差フィルムとして用いる場合、斜方蒸着された無機誘電体層の厚さは、蒸着物質の成長に異方性を生じて複屈折性を示す膜厚以上であれば特に制限されないが、下記計算式(3)

$$Ra = (n_{ax} - n_{ay}) \times da \quad (3)$$

〔式中、 n_{ax} は斜方蒸着層のフィルム面内の遅相軸方向の屈折率を、 n_{ay} は斜方蒸着層のフィルム面内の進相軸方向の屈折率を、 da は斜方蒸着層の厚みをそれぞれ示す。〕で示される無機誘電体の斜方蒸着層のフィルム面内のレターデーション値(Ra)が約10nm～200nmの範囲にある所定のレターデーション値が得ら

(5)

7

れる厚みとする。この厚みは、使用する物質（無機誘電体）の複屈折率と光学主軸のフィルム法線方向からの傾斜角度により異なるが、通常、約 $0.2\ \mu\text{m}$ ~ $5\ \mu\text{m}$ の範囲であり、好ましくは約 $0.4\ \mu\text{m}$ ~ $1\ \mu\text{m}$ の範囲で設定される。無機誘電体層の光学主軸のフィルム法線に対する傾斜角度や R_a 値の大きさ、透明高分子フィルムの R_b 値などは位相差フィルムを適用する用途により適宜変更して設定される。

【0026】斜方蒸着においてこのような厚みを得る方法としては、蒸着を多数回繰り返して多層膜とする方法も考えられる。しかし、このような装置で連続して斜方蒸着フィルムを作成した場合、図4に例示する垂直方向からの通常の蒸着で非晶質の等方層が形成されるのとは異なり、蒸着物質が図5に例示するような湾曲した柱状構造として成長し、多層膜とした場合には図6に例示するようにその界面が不連続面となるため、不要な干渉色が発生したり、耐久性試験において光学特性が大きく低下することがある。このため、フィルム上に連続して斜方蒸着層を形成する場合には1回の蒸着により単一層として斜方蒸着層を形成することが好ましい。この場合にはフィルムの搬送速度をさらに遅くすることが必要となるため、冷却板が不可欠であり、複数枚の冷却板を配置することがより好ましい。

【0027】ここでいう位相差フィルムの光学特性とは、位相差フィルムは通常偏光フィルムと積層して用いられることから、位相差フィルムのフィルム面内の遅相軸を偏光フィルムの吸収軸に対して 45° となるように貼合した場合の図7に示される光学系で測定されるクロスニコル下での分光透過率により $JIS-Z8722$ に基づいて算出される Y 値を意味する。この光学特性は、光学主軸がフィルム法線方向から 20° ~ 70° 傾斜していることにより発現する屈折率異方性に起因する R_a 値により決まるものであり、耐久性試験においてはこの値の変化により屈折率異方性の変化を代表させる。位相差フィルムの耐久性としては、 60°C 90% RH の高温高湿下に96時間放置した後の光学特性の残存率が 70% 以上であることが好ましく、残存率 80% であることがより好ましく、残存率 90% 以上であることがさらに好ましい。

【0028】本発明で用いる蒸着方法としては、電子ビーム蒸着法、イオンプレーティング法など公知の方法を用いることができる。生産性および耐久性の点から、電子ビーム蒸着法が好ましく用いられる。

【0029】また、冷却板、防着板およびキャンロールなどの冷却温度は、高分子のガラス転移温度未満であり、好ましくは熱変形温度未満であることが好ましいが、室温例えば 25°C 以下の冷媒を用いて冷却することがより好ましく、 0°C 以下の冷媒を用いて冷却することがさらに好ましい。

【0030】 Ta_2O_5 のように蒸着の際にタンタルと

8

酸素の組成比が崩れて酸素不足となって着色を起こすことがある物質を用いる場合には、必要に応じて蒸着機内に酸素ガスを導入して蒸着層中の酸素の組成比を調整して透明性を上げる手法を用いてもよい。

【0031】酸素ガスの導入量は、蒸着装置の容積と排気能力等により異なるため適宜選択される。導入量が少なすぎると酸素導入の効果が十分でなく、逆に導入量が多すぎる場合は気圧が上昇して蒸着速度が低下することがあるため注意が必要である。一般的には、装置内の気圧が 10^{-3}Torr より大きくならないように導入量を調節する。

【0032】本発明において、透明高分子フィルム上に無機誘電体の斜方蒸着層を設ける際、無機誘電体の斜方蒸着層と基材の透明高分子フィルムあるいは中間層を設けた透明高分子フィルムとの密着性を向上させるため、透明高分子フィルムおよび中間層の蒸着する側の表面に何らかの表面処理を施した後に蒸着を行うことも可能である。表面処理方法については特に限定されないが、一般的に用いられているものとしては真空中での加熱処理や、コロナ処理、イオンボンバード処理、プラズマ処理、紫外線照射、酸・アルカリ処理等を挙げることができる。表面処理方法や処理の程度は、使用する透明高分子フィルムや中間層、蒸着材料、および最終的に得られる位相差フィルムに必要な機械的強度、耐久性、光学特性により適宜選択される。

【0033】

【発明の効果】本発明により、非昇華性でかつ融点が 1000°C 以上である無機誘電体からなる蒸着材料を透明高分子フィルム上へ連続蒸着する際、特に位相差フィルムとして用いる蒸着層厚みが厚い蒸着フィルムを製造する場合際に、蒸着時の熱のために高分子フィルムの温度が上昇してフィルムが変形するなどの不具合が発生することなく、無機誘電体の蒸着層と透明高分子フィルムとの密着性や耐久性に優れた蒸着フィルムを連続して製造することができる。

【0034】

【実施例】以下、実施例により本発明を詳細に説明するが、本発明はこれに限定されるものではない。なお、実施例における R_a 値及び R_b 値の測定は、偏光顕微鏡を用いて波長 546nm の単色光で常法により行った。また、光学主軸のフィルム法線方向からの傾斜角度はフィルム面内の進相軸を傾斜軸とした時のレターデーション値（透明高分子フィルムが複屈折性を有する場合には透明高分子フィルムのレターデーション値を差し引いた値）の傾斜角依存性から、屈折率構造が一軸性であると仮定して当業者の常法により求めた。

【0035】耐久性試験には、本発明による位相差フィルムのフィルム面内の遅相軸が偏光フィルム（SQ-1852AP7、住友化学工業株式会社製）の吸収軸に対して 45° となるように、位相差フィルムの透明高分子

50

(6)

9

フィルム側に偏光フィルムを貼合し、斜方蒸着層側に光学的に等方なアクリル系粘着剤を介して厚さ1.1mmのガラス板を貼合した大きさが30mm×30mmのサンプルを用いた。

【0036】光学特性を求めるための分光透過率は、分光器(MCPD-2000、大塚電子株式会社製)を用いて図6に示した光学系にて入射光側の偏光プリズムとサンプルの偏光フィルムの吸収軸を平行として測定し、JIS-Z8722に基づきY値を算出した。Y値の初期値に対する、60℃90%RH下に96時間放置後のY値の割合を光学特性の残存率とした。なお、分光透過率のレファレンスは、偏光プリズムの吸収軸を平行として測定し、レファレンス測定後に偏光プリズムの吸収軸を直交にしてサンプルの測定を実施した。

【0037】実施例1

トリアセチルセルロースフィルム(商品名 フジTAC SH-80 富士写真フィルム(株)製、Rbは約11nm)上にコンマコーターにより紫外線硬化型のアクリル系樹脂をコート後、紫外線照射により硬化させて、中間層として厚さ約5μmのアクリル系樹脂膜を形成した透明高分子フィルムを得た。このフィルムを130mm幅にスリットした連続フィルムを得た。この透明高分子フィルムを図5の連続真空蒸着機内にセットし、気圧 1×10^{-4} Torrまで排気し、電子ビーム蒸着法により、蒸着開始角度80度、蒸着終了角度45度、蒸着中心角度60度、フィルムの蒸着中心と基板間の距離約350mm、となるように遮蔽板を配置し、その防着板と蒸着源の間に蒸着源からの輻射熱を防ぐ1枚の冷却板を設置し、EBガン出力6KW、搬送速度0.2m/分、キャンロールの冷却温度0℃、蒸着材料としてTa₂O₅を主成分としたTa(金属)との混合物(オプトロン社製、商品名:OA-100)を用いて、厚さ4700Åの単一層からなる斜方蒸着層を連続的に形成して位相差フィルムを得た。

【0038】この位相差フィルムの外観を目視により評価したところ、蒸着時の輻射熱による基材の変形もなく、またクラック等の蒸着層の剥離も認められなかった。この位相差フィルムはフィルム面内のレターデーション値が29nmであり、光学主軸は、連続蒸着時の蒸着角度の変化に対応してフィルム厚み方向に連続して変化しているが、変化していないものと仮定して求めた値はフィルム法線方向から約33度傾斜したものであった。この位相差フィルムを耐久性試験にかけたところ、光学特性の残存率は95%であった。

【0039】比較例1

実施例1と同様にして得た中間層を形成し表面処理を透明高分子フィルムを図5の連続真空蒸着機内にセットし、気圧 1×10^{-4} Torrまで排気し、電子ビーム蒸着法により、蒸着開始角度80度、蒸着終了角度45度、蒸着中心角度0度、フィルムの蒸着中心と基板間の

10

距離約325mm、となるように遮蔽板を配置し、EBガン出力6KW、搬送速度0.2m/分、キャンロールの冷却温度0℃で、蒸着材料としてTa₂O₅を主成分としたTa(金属)との混合物(オプトロン社製、商品名:OA-100)を用いて、厚さ3500Åの単一層からなる斜方蒸着層を連続的に形成して位相差フィルムを得た。

【0040】この位相差フィルムの外観を目視により評価したところ、蒸着時の輻射熱により基材が変形し、またTAC面に発泡も認められた。この位相差フィルムはフィルム面内のレターデーション値が16nmであり、光学主軸は、連続蒸着時の蒸着角度の変化に対応してフィルム厚み方向に連続して変化しているが、変化していないものと仮定して求めた値はフィルム法線方向から約27度傾斜したものであった。また、この位相差フィルムを耐久性試験にかけたところ、光学特性の残存率は36%と冷却板を設置して作製したものと比較して劣るものであった。

【図面の簡単な説明】

【図1】本発明による連続蒸着フィルムを製造するための第1の装置例の概略図。

【図2】本発明による連続蒸着フィルムを製造するための第2の装置例の概略図。

【図3】本発明による連続蒸着フィルムを製造するための第3の装置例の概略図。

【図4】図1に例示した垂直方向から蒸着する連続真空蒸着装置を用いて連続した透明高分子フィルム上に単一層からなる斜方蒸着層が形成されたフィルムの断面の模式図。

【図5】図2または図3に例示した斜方蒸着を行う連続真空蒸着装置を用いて連続した透明高分子フィルム上に単一層からなる斜方蒸着層が形成された位相差フィルムの断面の模式図。

【図6】図2または図3に例示した斜方蒸着を行う連続真空蒸着装置を用いて連続した透明高分子フィルム上に多層からなる斜方蒸着層が形成された位相差フィルムの断面の模式図。

【図7】位相差フィルムの光学特性の測定のための光学系の概略図。

【符号の説明】

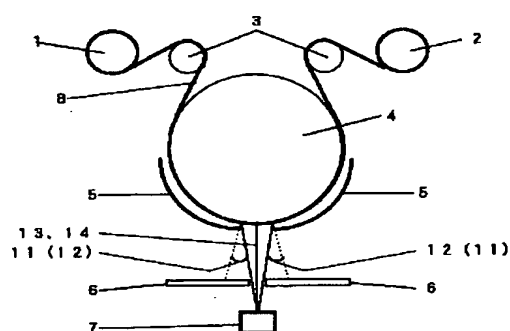
- 1 連続フィルム巻き出し部
- 2 連続フィルム書き取り部
- 3 ガイドロール
- 4 キャンロール
- 5 防着板
- 6 冷却板
- 7 蒸着源
- 8 透明高分子連続フィルム
- 11 蒸着開始角度
- 12 蒸着終了角度

(7)

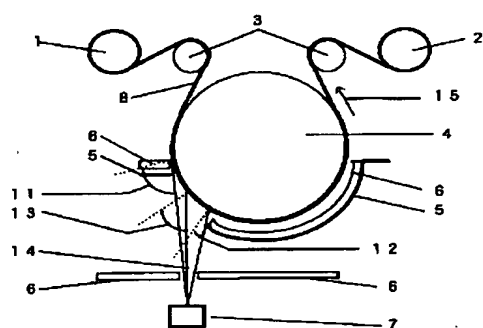
11

- 1 3 蒸着中心角度
1 4 蒸着源から引いた垂線
1 5 フィルム搬送方向
2 1 連続蒸着法による斜方蒸着層
2 2 中間層
2 3 透明高分子フィルム
5 1 入射光
5 2 入射光側の偏光プリズム
5 3 測定用サンプルの偏光フィルム
5 4 測定用サンプルの位相差フィルム

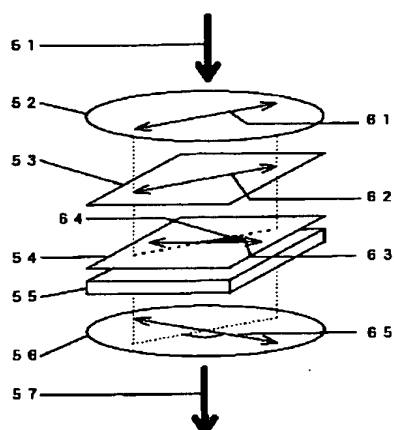
【図1】



【図3】



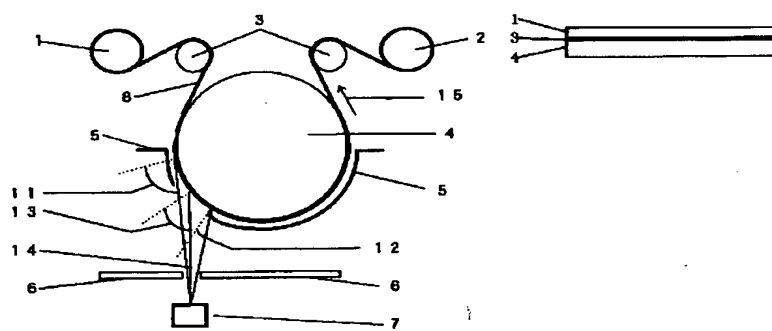
【図7】



12

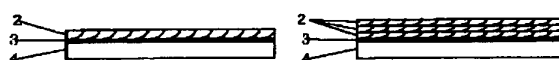
- 5 5 測定用サンプルを貼合したガラス板
5 6 出射光側の偏光プリズム
5 7 出射光
6 1 入射側の偏光プリズムの吸収軸方向
6 2 測定用サンプルの偏光フィルムの吸収軸方向
6 3 測定用サンプルの位相差フィルムのフィルム面内の遅相軸方向
6 4 測定用サンプルの偏光フィルムの吸収軸方向と位相差フィルムの遅相軸方向のなす角度 (4-5度)
6 5 出射光側の偏光プリズムの吸収軸方向

【図2】



【図5】

【図6】



【図4】

(8)

フロントページの続き

(51) Int. Cl. 6

C 0 8 J 7/06

G 0 2 F 1/1335

識別記号

C E P

C E Z

5 1 0

F I

C 0 8 J 7/06

G 0 2 F 1/1335

C E P Z

C E Z Z

5 1 0